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[54] MINIATURE QUADRUPOLE MASS SPECTROMETER ARRAY

[75] Inventors: **Ara Chutjian**, La Crescenta; **Michael H. Hecht**, Los Angeles; **Otto J. Orient**, Glendale, all of Calif.

[73] Assignee: **California Institute Of Technology**, Pasadena, Calif.

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,596,193.

[21] Appl. No.: **734,965**

[22] Filed: **Oct. 23, 1996**

Related U.S. Application Data

[62] Division of Ser. No. 540,817, Oct. 11, 1995, Pat. No. 5,596,193.

[51] **Int. Cl.**^{6} **H01J 49/42**

[52] **U.S. Cl.** **250/292**; 250/281

[58] **Field of Search** 250/292, 281

[56] **References Cited**

U.S. PATENT DOCUMENTS

5,596,193 1/1997 Chutjian et al. 250/292

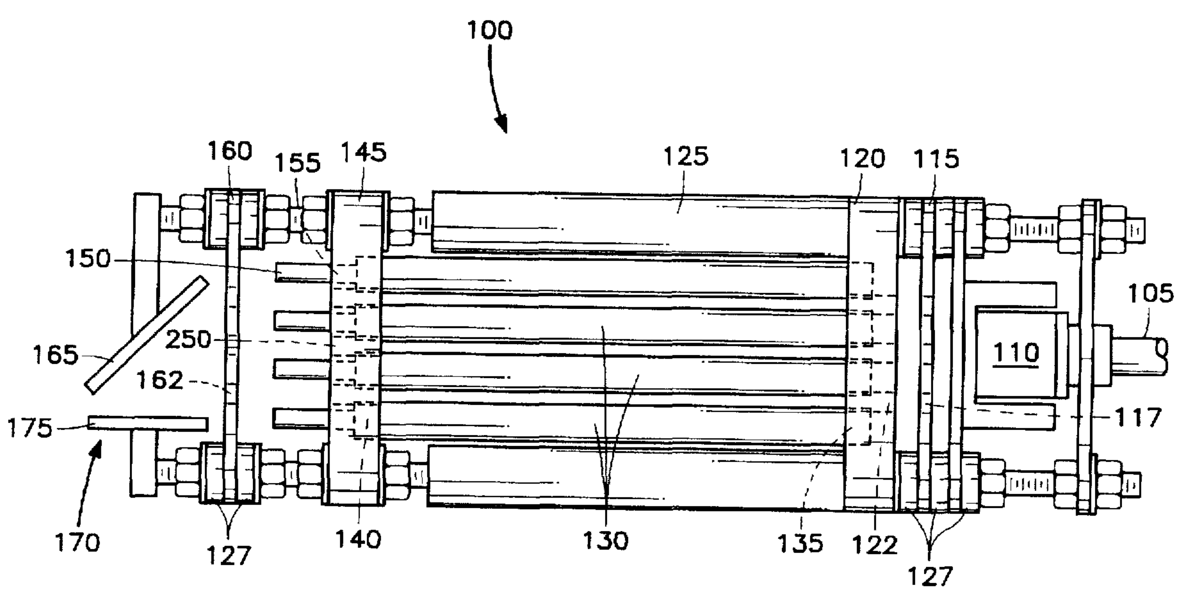
Primary Examiner—Jack I. Berman

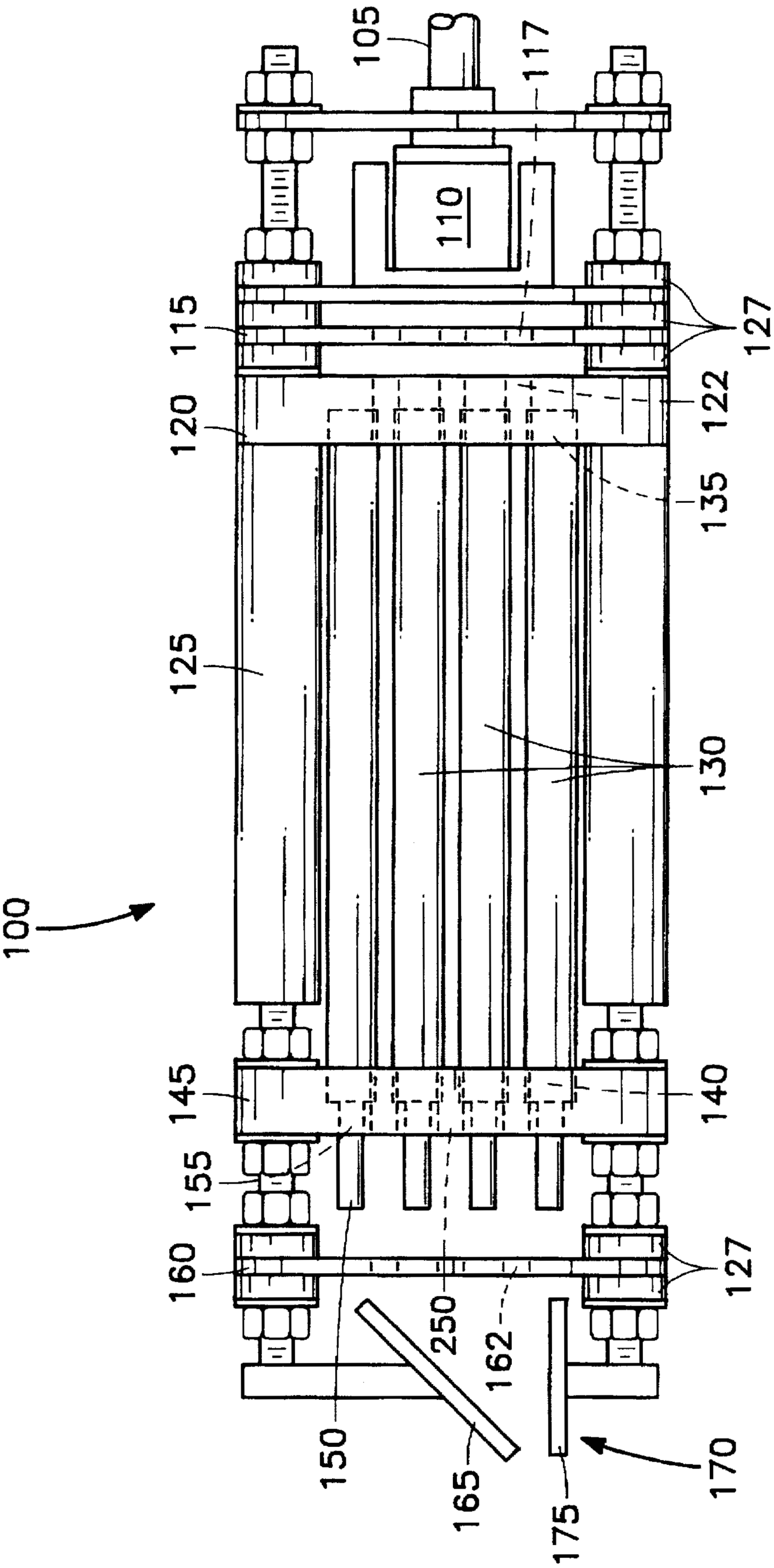
Attorney, Agent, or Firm—Michaelson & Wallace

[57] **ABSTRACT**

The present invention provides a minature quadrupole mass spectrometer array for the separation of ions, comprising a first pair of parallel, planar, nonmagnetic conducting rods each having an axis of symmetry, a second pair of planar, nonmagnetic conducting rods each having an axis of symmetry parallel to said first pair of rods and disposed such that a line perpendicular to each of said first axes of symmetry and a line perpendicular to each of said second axes of symmetry bisect each other and form a generally 90 degree angle. A nonconductive top positioning plate is positioned generally perpendicular to the first and second pairs of rods and has an aperture for ion entrance along an axis equidistant from each axis of symmetry of each of the parallel rods, a nonconductive bottom positioning plate is generally parallel to the top positioning plate and has an aperture for ion exit centered on an axis equidistant from each axis of symmetry of each of the parallel rods, means for maintaining a direct current voltage between the first and second pairs of rods, and means for applying a radio frequency voltage to the first and second pairs of rods.

33 Claims, 5 Drawing Sheets

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117
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170

FIG. 1

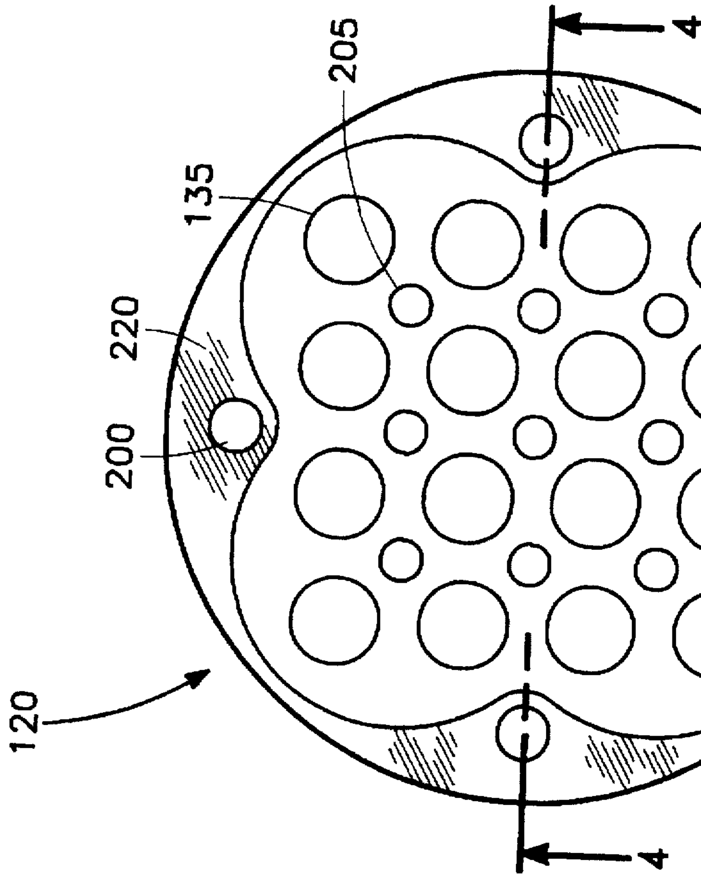


FIG. 3

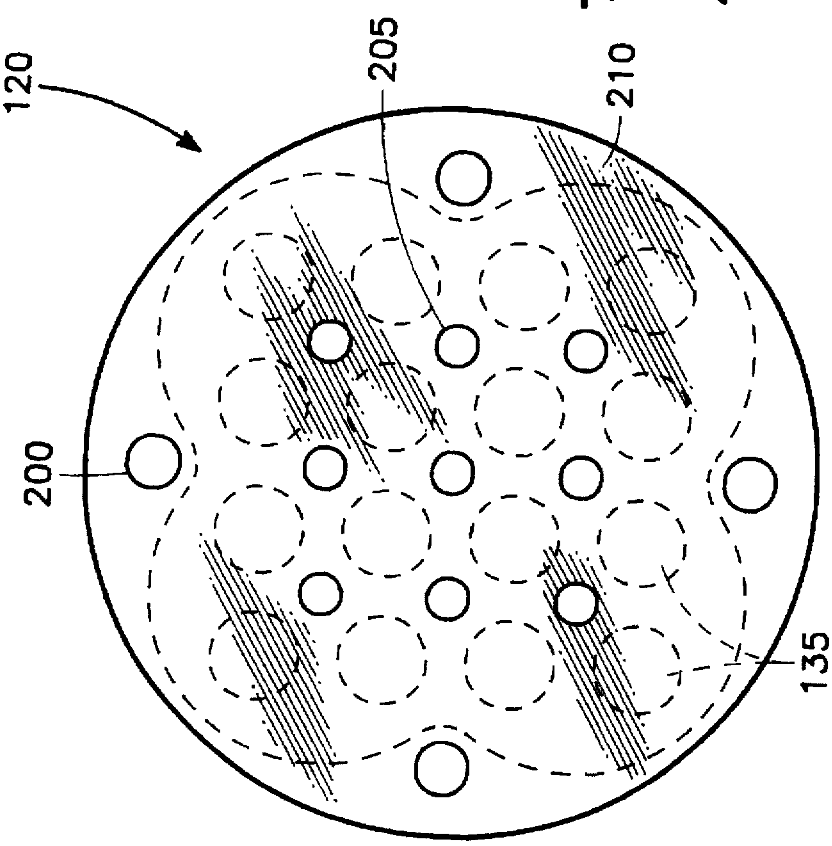


FIG. 2

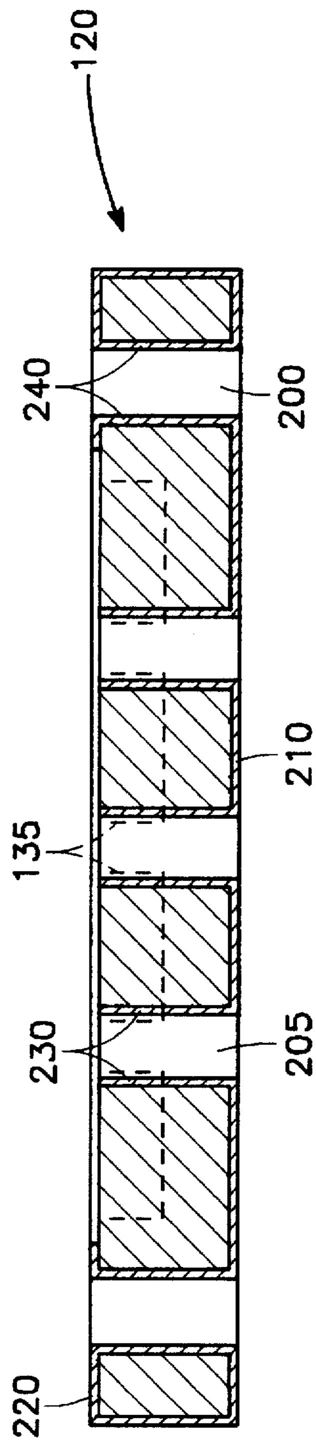


FIG. 4

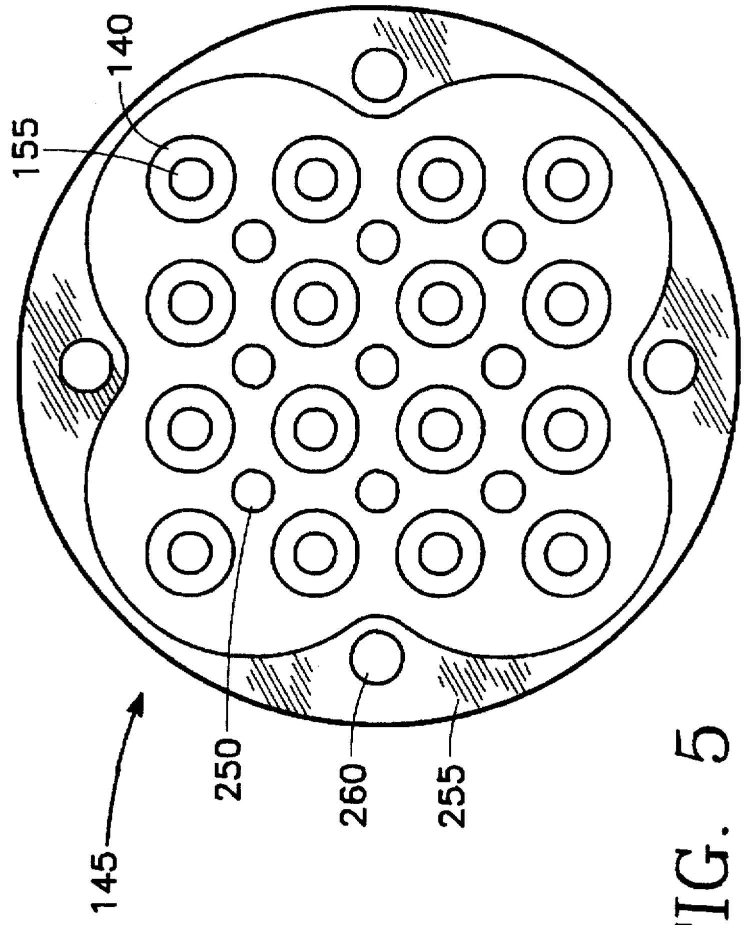


FIG. 5

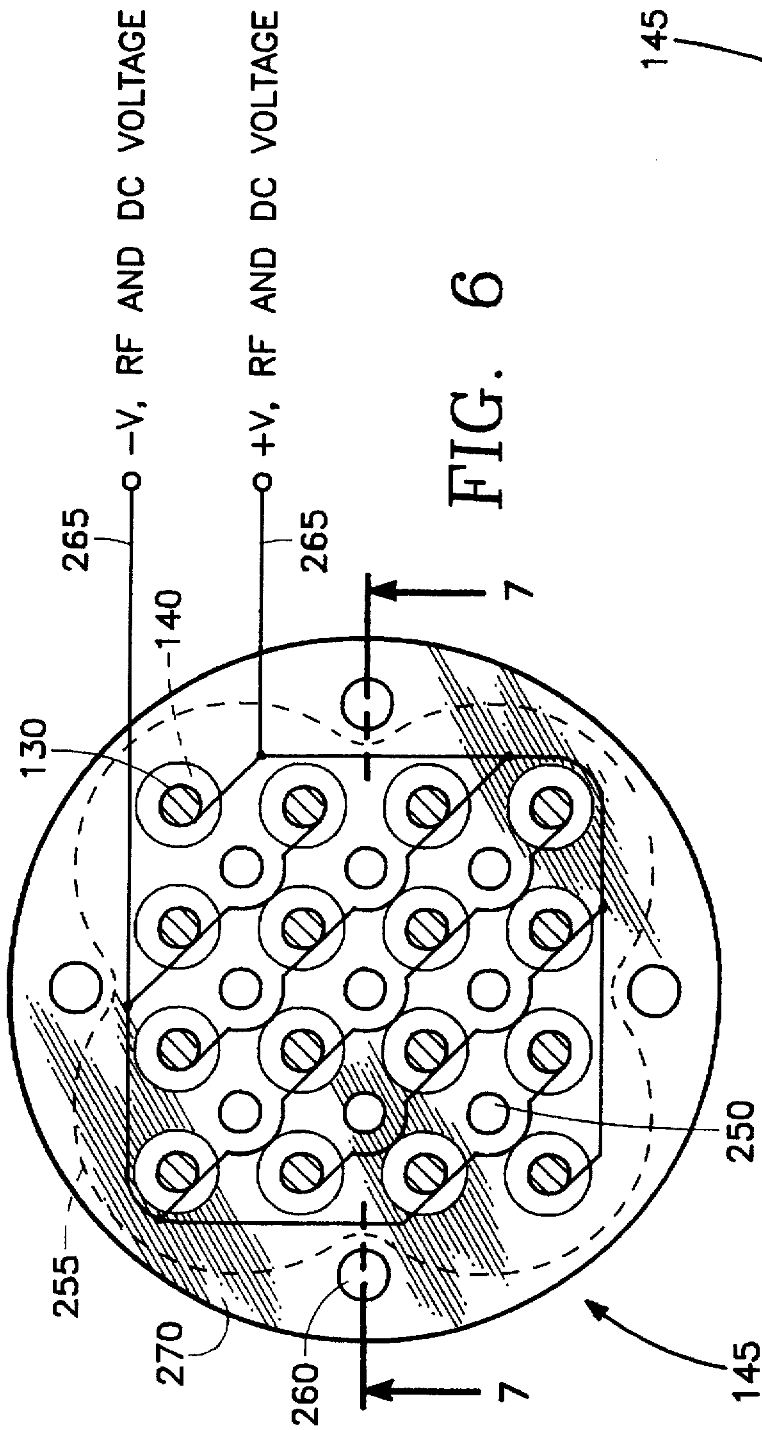
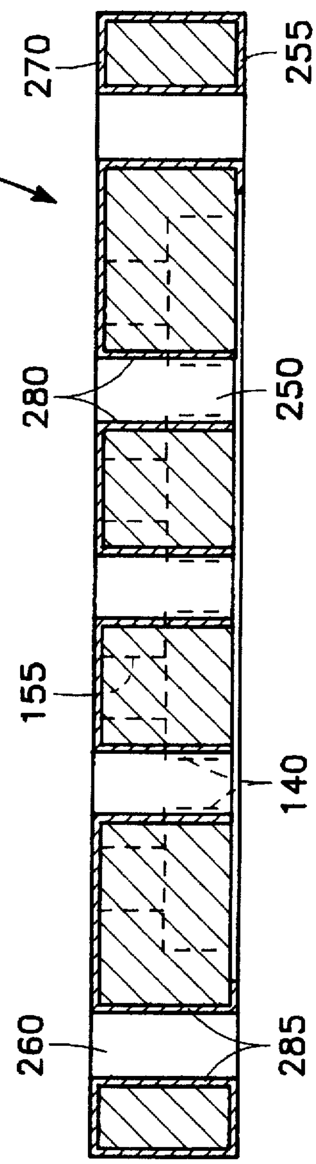

-V, RF AND DC VOLTAGE
+V, RF AND DC VOLTAGE
265
265
130
140
7
7
250
255
270
260
145

FIG. 6


270
255
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280
250
155
140
260
285

FIG. 7

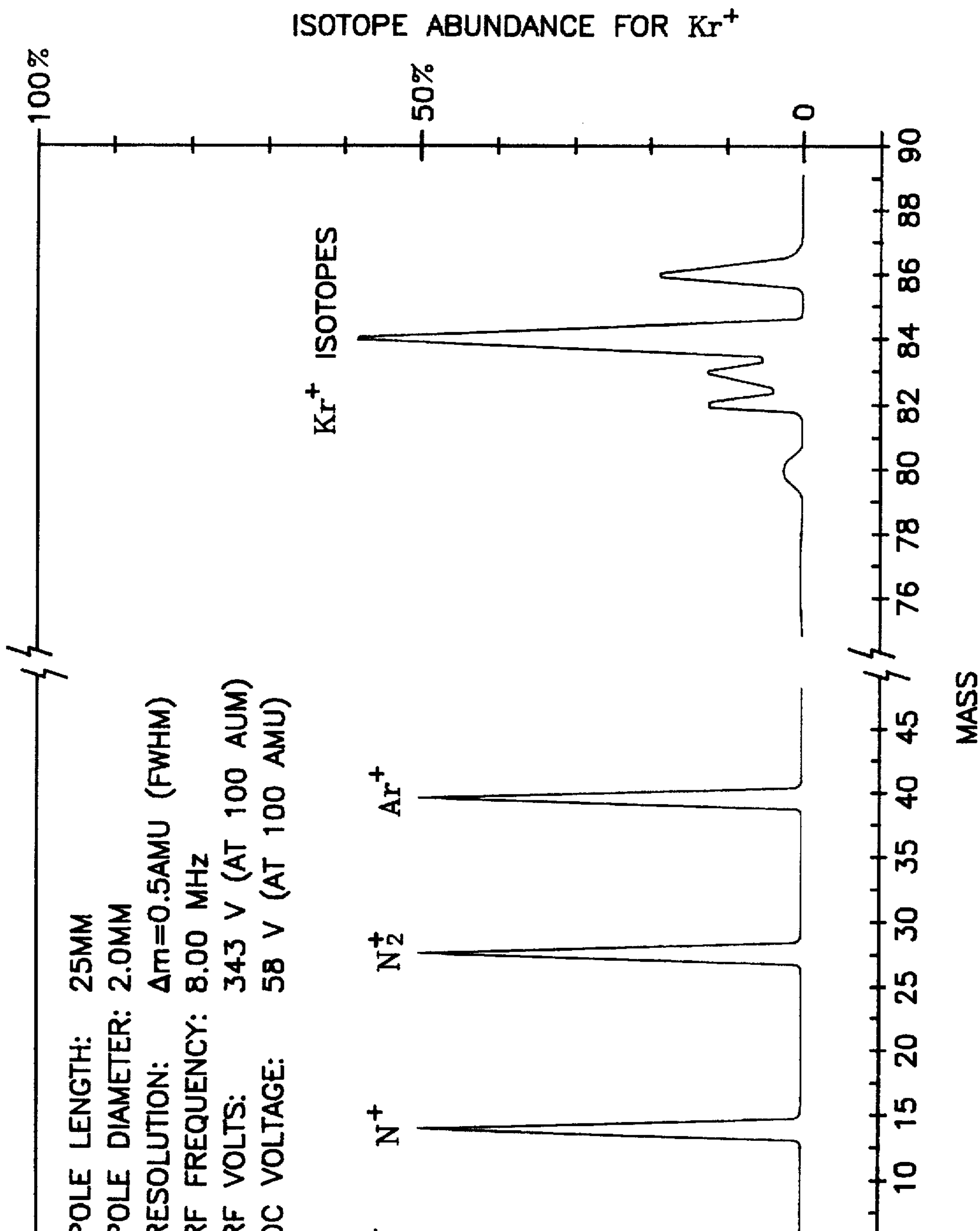
ISOTOPE ABUNDANCE FOR Kr^+
100%
50%
0
Kr^+ ISOTOPES
POLE LENGTH: 25MM
POLE DIAMETER: 2.0MM
RESOLUTION: Δm=0.5AMU (FWHM)
RF FREQUENCY: 8.00 MHz
RF VOLTS: 343 V (AT 100 AUM)
DC VOLTAGE: 58 V (AT 100 AMU)
He^+
N^+
N_2^+
Ar^+
1.0
0.5
0.0
0 5 10 15 20 25 30 35 40 45 76 78 80 82 84 86 88 90
MASS
RELATIVE INTENSITIES [He^+, N^+, N_2^+, Ar^+]

FIG. 8

MINIATURE QUADRUPOLE MASS SPECTROMETER ARRAY

This is a division of application Ser. No. 08/540,817, filed Oct. 11, 1995, now U.S. Pat. No. 5,596,193.

ORIGIN OF INVENTION

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

BACKGROUND OF THE INVENTION

1. Technical Field

The present invention relates to an improved quadrupole mass spectrometer array for the separation of ions with different masses.

2. Background Art

The quadrupole mass spectrometer ("QMS") was first proposed by W. Paul (1958). In general, the QMS separates ions with different masses by applying a direct current ("dc") voltage and a radio frequency ("rf") voltage on four rods having hyperbolic or circular cross sections and an axis equidistant from each rod. Opposite rods have identical potentials. The electric potential in the quadrupole is a quadratic function of the coordinates.

Ions are introduced in a longitudinal direction through a circular entrance aperture at the ends of the rods and centered on a midpoint between rods. Ions are deflected by the field depending on the ratio of the ion mass to the charge of the ion ("mass/charge ratio") and, by selecting the applied voltage and the amplitude and frequency of the rf signal, only ions of a selected mass/charge ratio exit the QMS along the axis of a quadrupole at the opposite end and are detected. Ions having other mass/charge ratios either impact the rods and are neutralized or deflected away from the axis of the quadrupole. As explained in Boumsellek, et al. (1993), a solution of Mathieu's differential equations of motion in the case of round rods provides that to select ions with a mass m, using an rf signal of frequency f and rods separated by a distance R_o, the peak rf voltage V_o and dc voltage U_o should be as follows:

$$V_o=7.219\ m\ f^2\ R_o^2$$

$$U_o=1.212\ m\ f^2\ R_o^2$$

Conventional QMSs weigh several kilograms, have volumes of the order of 10^3 cm^3, and require 10–100 watts of power. Further, vacua in the range of 10^{-6}–10^{-8} torr are needed for satisfactory signal-to-noise ratio, due to the large free mean path required to transverse the pole length. Commercial QMSs of this design have been used for characterizing trace components in the atmosphere (environmental monitoring), in automobile exhausts, thin film manufacture, plasma processing, and explosives/controlled-substances detection. Such conventional QMSs are not suitable, however, for spacecraft life support-support systems and certain national defense missions where they have the disadvantages of relatively large mass, volume, and power requirements.

To meet these needs, a miniature QMS was developed by Ferran Scientific, Inc. (San Diego, Calif.). The Ferran QMS uses a miniature array of sixteen rods comprising nine individual quadrupoles. The rods are supported only at the detector end of the QMS by means of powdered glass that is heated and cooled to form a solid support structure. The dc and rf electric potentials are applied by the use of springs contacting the rods. The Ferran QMS dimensions are approximately 2 cm diameter by 5 cm long, including a gas ionizer and detector, with an estimated mass of 50 grams. The reduced size of the Ferran QMS results in several advantages, including a reduced power consumption of approximately 10 watts and the ability to operate at a higher operating pressure of approximately 1 mTorr.

The Ferran QMS was analyzed by Boumsellek, et al. (1993) and it was determined that its resolution was approximately 2.5 amu in the mass range 1–95 amu. This is a relatively low resolution for a QMS, making the miniature Ferran QMS only useful for commercial processing (e.g. chemical-vapor deposition, blood-plasma monitoring), but not for applications that require accurate mass separation, such as spacecraft life-support systems. The low resolution was traced to the fact that the rods were aligned only to within a ±4% accuracy, whereas an alignment accuracy in the range of 0.1% is necessary for a high resolution QMS (Boumsellek et al. 1993). Alternatively, the ratio of rod radius to one-half the distance between rods having the same polarity (the "kissing circle" radius) of the Ferran QMS was measured to vary in the range 1.10–1.20, whereas one design ratio is 1.160+0.1% (Boumsellek et al. 1993). It is these and other disadvantages of the Ferran QMS that the present invention overcomes.

SUMMARY OF THE INVENTION

The quadrupole mass spectrometer array ("QMSA") of the present invention retains the size, weight, vacuum operating conditions and power consumption advantages of the Ferran QMS, while significantly improving its resolution and mass range for measurements of ion mass. A QMSA according to the invention comprises a first pair of parallel, planar, nonmagnetic conducting rods each having an axis of symmetry, a second pair of planar, nonmagnetic conducting rods each having an axis of symmetry parallel to said first pair of rods and disposed such that a line perpendicular to each of said first axes of symmetry and a line perpendicular to each of said second axes of symmetry bisect each other and form a generally 90 degree angle. A nonconductive top positioning plate is positioned generally perpendicular to the pairs of rods and has an aperture for ion entrance along an axis equidistant from each axis of symmetry of each of the parallel rods, a nonconductive bottom positioning plate is generally parallel to the top positioning plate and has an aperture for ion exit centered on an axis equidistant from each axis of symmetry of each of the parallel rods, means for maintaining a direct current voltage difference between the first and second pairs of rods, and means for applying a radio frequency voltage to said first and second pairs of rods.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross section view of a QMSA according to the present invention.

FIG. **2** is a top view of the top retainer plate of the QMSA of FIG. **1**.

FIG. **3** is a bottom view of the top retainer plate of FIG. **2**.

FIG. **4** is a side view of the top retainer plate of the QMSA of FIG. **1**.

FIG. **5** is a top view of the bottom retainer plate of the QMSA of FIG. **1**.

FIG. **6** is a bottom view of the bottom retainer plate of FIG. **5**.

in FIG. 6, such as by spot welding wires to the ends of rods **130**. Other suitable means may be used to impart the voltages to rods **130**, but the means selected should not cause the rods **130** to move or impart a stress to the rods **130** that could cause movement, such as the springs used in the QMS made by Ferran. Any tendency to move the rods **130** imparted by the means to apply the electric potentials can result in misalignment of the rods **130** and reduce resolution of the QMSA.

After the selected ions pass through the apertures **250**, they are focused by a conventional ion optical grid **160** (shown in FIG. 1) having an applied potential of approximately 100–200 dc volts. After focusing, the ion beam is deflected by the ion deflector plate **165** onto the particle detector **170**, such as a Faraday cup, microchannel plate, or channeltron multiplier (made by Gallileo Electro-Optics Corporation, Sturbridge, Mass.), to detect the selected ions.

A QMSA according to the invention was tested using a standard electron-impact ionizer and an iridium filament for the ionization chamber **110**. A channeltron multiplier was used as the particle detector **170** in conjunction with a computer interface module that produced a display of the relative intensity of the detector output versus ion mass. A scan of rf and dc voltages was performed to detect corresponding mass units. The rf voltage was varied from 0 to 1,000 volts at a frequency of 8 MHz, and the dc voltage was varied from 0 to 160 volts to sweep the QMSA over a mass range of from 0 to 100 amu. Greater rf voltages (up to 2000 volts) and dc voltages (up to 350 volts), and a range of rf frequencies (from 4 to 12 MHz) may be used to detect ions with a greater atomic mass.

The resolution and sensitivity of the QMSA was directly measured from the digitized output. The digital measuring routine utilized the measurements around a single mass peak to calculate mass position and intensity. The output signal shown in FIG. 8 is helium (mass 4), nitrogen (mass 14), nitrogen molecule (mass 28), argon (mass 40) and several isotopes of krypton (maximum isotope abundance at mass 84) at a pressure of 1.0×10^{-7} Torr. The full width at half maximum (FWHM) of these peaks is approximately 0.5 amu. Based on the data of FIG. 8 and the data reported by Boumsellek, et al. (1993), the QMSA of the invention exhibits the following substantial improvements in minimum detectable density (expressed in cm^{-3}) over the Ferran QMS:

	QMSA of Invention	Ferran QMS
Neutral particles	10^4–10^{12}	10^8–10^{14}
Ions	10^0–10^8	10^4–10^{10}

As mentioned earlier, the number of quadrupoles can be increased by increasing the number of rods, to form a quadrupole array or QMSA. This has the effect of increasing the sensitivity and dynamic range of the QMS. A limit on improving performance in this manner is the physical size of the QMSA.

To summarize, a miniature QMSA of the invention achieved a mass resolution of 0.5 amu or better, which is accurate enough to make it a useful as a mass analyzer. Further, the sensitivity of the QMSA of the invention is at least 4 orders of magnitude greater than the previous Ferran QMS, which significantly extends the lower operating limits of a QMS. The QMS of the invention also exhibits a dynamic range of 2 orders of magnitude better than the Ferran device, which substantially extends the operational

range of a QMS. These advantages result from novel features of the invention, including the use of top and bottom positioning plates to enhance rod alignment, conductive layers on the plates to avoid surface charging, electrical connections to the rods that reduce stress on the rods that introduces alignment error, and use of a particle multiplier.

Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

What is claimed is:

1. A quadrupole mass analyzer for the separation of ions, comprising:

- a first pair of parallel, planar, nonmagnetic conducting rods, each having an axis of symmetry;
- a second pair of planar, nonmagnetic conducting rods each having an axis of symmetry parallel to said first pair of rods and disposed such that a line perpendicular to each of said first axes of symmetry and a line perpendicular to each of said second axes of symmetry bisect each other and from a generally 90 degree angle;
- a nonconductive top positioning plate generally perpendicular to said first and second pairs of rods and having an aperture for ion entrance along an axis equidistant from each of said axes of symmetry;
- a nonconductive bottom positioning plate generally parallel to said top positioning plate and having an aperture for ion exit centered on an axis equidistant from each of said axes of symmetry;
- means for maintaining a direct current voltage between said first and second pairs of rods; and
- means for applying a radio frequency voltage to said first and second pairs of rods;
- wherein said positioning plates further comprise means for preventing charging of exterior and interior surfaces of said plates.

2. The analyzer of claim **1** wherein said top positioning plate further comprises a conductive layer covering the interior surface of said aperture and a face of said top positioning plate opposite said rods.

3. The analyzer of claim **1** wherein said bottom positioning plate further comprises a conductive layer covering the interior surface of said aperture and a face of said bottom positioning plate opposite said rods.

4. The analyzer of claim **1** wherein said first and second pairs of rods have approximately equal lengths.

5. The analyzer of claim **4** wherein said equal length is no greater than approximately 2 cm.

6. The analyzer of claim **1** wherein said first and second pairs of rods have approximately equal radii.

7. The analyzer of claim **6** wherein said equal radius is no greater than approximately 0.1 cm.

8. The analyzer of claim **6** wherein the ratio between said radius and one-half the distance between surfaces of said pairs of rods is approximately 1.16.

9. The analyzer of claim **1** wherein the direct current voltage between said first and second pair of rods is in the range of more than 0 volts to approximately 350 volts.

10. The analyzer of claim **1** wherein the radio frequency voltage applied to said first and second pair of rods is in a frequency range of approximately 4 to 12 MHz.

11. The analyzer of claim **1** wherein the radio frequency voltage applied to said first and second pair of rods is in the range of more than 0 volts to approximately 2,000 volts.

12. The analyzer of claim **1** further comprising an electrode disposed adjacent a face of said top positioning plate

opposite said rods and having an aperture along an axis equidistant from each axis of symmetry of each of said parallel rods.

13. The analyzer of claim **1** further comprising a grid disposed adjacent a face of said bottom positioning plate opposite said rods and having an aperture along an axis equidistant from each axis of symmetry of each of said parallel rods.

14. The analyzer of claim **13** further comprising an ion deflector plate disposed adjacent said grid opposite bottom positioning plate and at an angle to said grid.

15. The analyzer of claim **14** wherein said angle is approximately 45 degrees.

16. The analyzer of claim **1** wherein said means for maintaining a direct current voltage and said radio frequency means do not displace said rods.

17. The analyzer of claim **16** wherein said means for maintaining a direct current voltage and said radio frequency means comprise spot welds to maintain an electrical connection with said rods.

18. The analyzer of claim **1** further comprising a plurality of said first and second pairs of rods wherein a red of each first pair comprises a rod of another first pair and a rod of each second pair comprises a rod of another second pair.

19. A quadrupole mass analyzer for the separation of ions, comprising:

a set of four parallel, nonmagnetic, conducting rods, each having an axis of symmetry, disposed such that coplanar lines connecting each said axis and intersecting only at said axes form a generally square figure;

a nonconductive top positioning plate generally perpendicular to said set of rods and having an aperture along an axis equidistant from each axis of symmetry of each of said parallel rods;

a nonconductive bottom positioning plate generally parallel to said top positioning plate and having an aperture centered on an axis equidistant from each axis of symmetry of each of said parallel rods;

means for maintaining a direct current voltage between a first opposite pair of said rods and a second opposite pair of said rods; and

means for applying a radio frequency voltage to a first opposite pair of said rods and a second opposite pair of said rods;

wherein said positioning plates further comprise means for preventing charging of exterior and interior surfaces of said plates.

20. The analyzer of claim **19** wherein said top positioning plate further comprises a conductive layer covering the interior surface of said aperture and a face of said top positioning plate opposite said rods.

21. The analyzer of claim **19** wherein said bottom positioning plate further comprises a conductive layer covering the interior surface of said aperture and a face of said bottom positioning plate opposite said rods.

22. The analyzer of claim **19** wherein said means for maintaining a direct current voltage and said radio frequency means do not displace said rods.

23. The analyzer of claim **22** wherein said means for maintaining a direct current voltage and said radio frequency means comprise spot welds to maintain electrical connection with said rods.

24. A method for separating ions with a quadrupole mass analyzer having a first pair of parallel, planar, nonmagnetic conducting rods, each having an axis of symmetry, said method comprising the steps of:

positioning a second pair of planar, nonmagnetic conducting rods, each having an axis of symmetry parallel to said first pair of rods, such that a line perpendicular to each of said first axes of symmetry and a line perpendicular to each of said second axes of symmetry bisect each other and form a generally 90 degree angle;

arranging a nonconductive top positioning plate in a perpendicular relationship with said first and second pairs of rods, said nonconductive top positioning plate has an aperture for ion entrance along an axis equidistant from each of said axes of symmetry;

arranging a nonconductive bottom positioning plate in a parallel relationship with said top positioning plate, said nonconductive bottom positioning plate has an aperture for ion exit centered on an axis equidistant from each of said axes of symmetry;

maintaining a direct current voltage between said first and second pairs of rods;

applying a radio frequency voltage to said first and second pairs of rods; and

preventing charging of exterior and interior surfaces of said plates.

25. The method of claim **24** wherein said maintaining step comprises maintaining a direct current voltage between said first and second pairs of rods with a rigid and non-deforming device and wherein said applying step comprises applying a radio frequency voltage to said first and second pairs of rods with a rigid and non-deforming device.

26. The method of claim **24** further comprising the step of covering the interior surface of said aperture and a face of said top positioning plate opposite said rods with a conductive layer.

27. The method of claim **24** further comprising the step of covering the interior surface of said aperture and a face of said bottom positioning plate opposite said rods with a conductive layer.

28. The method of claim **24** further comprising the step of disposing an electrode adjacent a face of said top positioning plate opposite said rods, wherein said electrode has an aperture along an axis equidistant from each axis of symmetry of each of said parallel rods.

29. The method of claim **24** further comprising the step of disposing a grid adjacent a face of said bottom positioning plate opposite said rods, wherein said grid has an aperture along an axis equidistant from each axis of symmetry of each of said parallel rods.

30. The method of claim **29** further comprising the step of disposing an ion deflector plate adjacent said grid opposite bottom positioning plate and at an angle to said grid.

31. The method of claim **30** wherein said angle is approximately 45 degrees.

32. The method of claim **24** further comprising the step of preventing said step of maintaining a direct current voltage and said step of applying a radio frequency voltage from displacing said rods.

33. The method of claim **24** further comprising the step of providing a plurality of said first and second pairs of rods, wherein a rod of each first pair comprises a rod of another first pair and a rod of each second pair comprises a rod of another second pair.

* * * * *